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Plutonium(IV) Sorption to Montmorillonite in the Presence of Organic Matter

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Abstract

The effect of altering the order of addition in a ternary system of plutonium(IV), organic matter (fulvic acid, humic acid and desferrioxamine B), and montmorillonite was investigated. A decrease in Pu(IV) sorption to montmorillonite in the presence of fulvic and humic acid relative to the binary Pu-montmorillonite system, is attributed to strong organic aqueous complex formation with aqueous Pu(IV). No dependence on the order of addition was observed. In contrast, in the system where Pu(IV) was equilibrated with desferrioxamine B (DFOB) prior to addition of montmorillonite, an increase in Pu(IV) sorption was observed relative to the binary system. When DFOB was equilibrated with montmorillonite prior to addition of Pu(IV), Pu(IV) sorption was equivalent to the binary system. X-ray diffraction and transmission electron microscopy revealed that DFOB accumulated in the interlayer of montmorillonite. The order of DFOB addition plays an important role in the observed sorption/desorption behavior of Pu. The irreversible nature of DFOB accumulation in the montmorillonite interlayer leads to an apparent dependence of Pu sorption on the order of addition in the ternary system. This work demonstrates that the order of addition will be relevant in ternary systems in which at least one component exhibits irreversible sorption behavior.

Keywords: Plutonium, Colloids, Humic acid, Siderophore, Sorption, Clay

1.0 Introduction

Decades of nuclear weapons production and testing, disposal of nuclear material, scheduled and accidental discharges from nuclear power reactors have all lead to plutonium (Pu) being introduced into the environment. For instance, approximately 4.8×10^{18} Bq of Pu have been released into the subsurface at the Nevada National Security Site, Nevada USA¹. The large quantities of Pu present in the environment combined with its radiological and chemical toxicity² and long half-life (^{239}Pu $t_{1/2} = 2.4 \times 10^4$) make understanding and predicting the fate of Pu in the environment important.

Sorption of Pu to montmorillonite is of particular importance as clays are ubiquitous in the environment. In addition, bentonite, composed primarily of montmorillonite, has been proposed as a backfill material for long-term radioactive waste disposal sites in many countries. While Pu sorption to montmorillonite may lead to immobilization of Pu, sorption of Pu to inorganic colloidal matter^{3,4} (including montmorillonite) as well as natural organic matter⁵ has been linked to increases in Pu environmental mobility. Thus Pu sorption to montmorillonite may lead to immobilization and/or mobilization depending on the nature and conditions of Pu interaction with montmorillonite.

The behavior of Pu on mineral and organic surfaces is a function of its oxidation state, where Pu is known to exist primarily in the IV and V oxidation states in natural waters⁶. Previous studies have observed reduction of Pu(V) to Pu(IV) on the surface of montmorillonite⁷, though the rates are far slower than those of iron minerals^{8,9}. Sorption of Pu(IV) to montmorillonite has been shown to be linear over 10 orders of magnitude in Pu concentration.¹⁰ Under atmospheric low ionic strength conditions, sorption is highest at pH 4 and decreases as pH increases (**Table 1**).

Humic substances are large organic molecules derived from the degradation of organic matter in the environment. Two major classifications of humic substances are humic acid (HA) and fulvic acid (FA), which are operationally differentiated by the pH range in which they are soluble. FA is soluble at all pH while HA is insoluble at low pH. In addition to solubility, HA has greater carbon content and is generally larger than FA. Humic substances play an important role in the transport of metals in the environment and studies of nuclear fallout in Japan and Korea have found that up to 60% of Pu was associated with HA and FA^{11,12}.

As a tool for solubilizing iron necessary for metabolic activity, many bacteria and fungi produce strong chelators called siderophores. With few exceptions, fungal siderophores contain hydroxamic acid functional groups¹³, giving them a distinct chemical difference to the carboxylic acid functional groups of humic and fulvic acid. Siderophores are known to form soluble complexes with more than just iron, and increases in Pu oxide dissolution have been observed in the presence of naturally occurring siderophores¹⁴. One commonly studied siderophore is desferrioxamine B (DFOB); consisting of three

hydroxamic acids linked by succinic acid and diaminopentane chains (**Figure 1**). DFOB is critical for iron acquisition in a variety of cell strains¹⁵ and select microbes have been shown to produce up to 0.136 mM DFOB in iron deficient environments¹⁶. In metal-free solutions, DFOB exists primarily as a linear chain, though upon complexation with most metals it forms a cyclical complex¹⁷. The tendency to form cyclical multidentate complexes results in very strong complexes, such as those of Fe^{III} and Pu(IV) (**Table 1**)¹⁸. DFOB is attributed to decreases in metal sorption to zeolites¹⁹, kaolinite²⁰, and iron minerals²⁰, while increases in sorption have been observed with swelling clays^{20,21}.

Experiments where the order of addition of metal, ligand, and mineral are examined are generally limited to HA and FA, of which no consensus in the literature on its importance has been reached. For instance, No effect was also observed with thorium, an analog for Pu, for the Th(IV)-HA-bentonite system²², while up to a 90% difference in Th(IV) sorption was observed for Th(IV)-HA-hematite system²³. In the case of the Pu(IV)-HA-kaolinite system, order of addition had no effect²⁴. However, in both the Pu(IV)-HA-kaolinite and Th(IV)-HA-bentonite systems, an increase in sorption at low pH in the presence of humic substances was observed and attributed to surface ternary complexes. Order of addition effects in the Cm(III)-HA-silica system varied with pH and were partially attributed to Cm(III) incorporation into the silica²⁵. Sorption of Ni(II) in the Ni(II)-HA/FA-montmorillonite system showed no effect in the order of addition²⁶. Alternatively in the Ni(II)-FA-bohemite (γ -AlO(OH)) system order of addition did not affect surface sorption on the macroscale, but different amounts of the surface species Ni(II)-FA-AlOOH and FA-Ni(II)-AlOOH were observed by Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy²⁷. The different Ni(II)-FA-bohemite surface complexes were investigated at 250 mg/L fulvic acid. At these concentrations, FA is known to form high molecular weight aggregates, which may not reflect the chemistry of the smaller molecules present at lower concentrations. No studies examining the order of addition of DFOB are present in the literature to date. However, order of addition of arginine, a nitrogen containing small ligand, had an effect on Ni(II) sorption to a loamy sand while the carboxylic acid containing citrate showed no effect²⁸.

Thermodynamic stability constants of Pu(IV)-organic complexes, and some comparable Fe(III) complexes, used in our studies are shown in **Table 1**. Binding constants of

Pu(IV)-HA have been determined using HA immobilized on silica gel and ultrafiltration, resulting in different apparent binding constants^{29,30}. The representation of the thermodynamic data differs by almost ten orders of magnitude. However, when the thermodynamic data are adjusted for the differences in complex formed (e.g Pu(IV)HA vs. Pu(IV)(OH)₃HA) they are in better agreement. For the sake of simplicity, the HA complex of Pu(IV) is referred to as Pu(IV)HA in this manuscript, the most recent complexation data of Zimmerman *et. al.* were used in our speciation model. In the presence of HA, Pu(V) and Pu(VI) are known to reduce to Pu(IV)^{31,32}. This reduction simplifies speciation calculations as it can be assumed that Pu(IV) is the only oxidation state present in our ternary sorption experiments.

In this paper, we present the results of a study investigating the sorption of Pu(IV) to montmorillonite in the presence of three types of organic matter (HA, FA, and DFOB). The order of organic matter addition was investigated to determine if order of addition may influence Pu(IV) sorption characteristics. In addition, transmission electron microscopy (TEM) and x-ray diffraction (XRD) were employed to examine whether sorption of organic matter can lead to changes in the morphology and interlayer structure of montmorillonite.

2.0 Methods

Unless otherwise noted all chemicals were of high purity (reagent grade) and used without any additional purification. A ²³⁸Pu (98.9% ²³⁸Pu, 0.11% ²⁴¹Pu, and 0.1% ²³⁹Pu by activity) stock was prepared for all experiments. Impurities were removed by loading Pu onto a Bio Rad AG 1-8X resin, in 8M HNO₃, and eluting as Pu(III) with a HI:HCl mixture. The eluent was heated to dryness several times to remove excess HI and subsequently dissolved in 1.0N HCl. The oxidation state of the Pu stock solution was verified by UV-Vis and LaF₃ precipitation³³ to be IV (99%). ²³⁸Pu concentrations were determined by Liquid Scintillation Counting (Packard Tri-Carb TR2900 LSA) for all experiments.

Preparation of montmorillonite colloids from SWy-1 (Source Clays Repository of the Clay Minerals Society) used in this study is described in Zavarin *et. al.*, 2012⁷. Briefly, montmorillonite was treated with 1 mM HCl and 30 mM H₂O₂ to remove salts and limit

redox active species. The clay was homoionized with 10 mM NaCl and dialized in >18 MΩ water (Milli-Q Gradient System). After homoionization, the clay was suspended in >18 MΩ water and centrifuged at 180 g for 5 minutes to sediment particles >2 μm. The remaining supernatant was then centrifuged at 2500 g for 6 hours to sediment all particles <50 nm. The suspension was dried at 40 °C and solutions of 10 g/mL montmorillonite were prepared in NaCl/NaHCO₃. The surface area and iron content of SWy-1 Na-montmorillonite prepared under these conditions was previously determined to be $31.5 \pm 0.17 \text{ m}^2$ and $9.5 \pm 0.6 \times 10^{-6} \text{ mol}_{\text{Fe}}/\text{g}_{\text{clay}}$, respectively¹⁰. Considering possible soluble Fe(III) and Fe(III) organic complexes, under the conditions of our experiments an excess of uncomplexed ligand will be present.

Elliot Soil HA standard and Suwannee River FA were purchased from the International Humic Substances Society and used with no further purification. Solid HA/FA was dissolved in 0.002 M freshly prepared NaOH to reach 100 ppm in carbon. Desferrioxamine B mesylate (Sigma-Aldrich) was dissolved in >18 MΩ water to reach 100 ppm C. All solutions were made fresh monthly and stored in amber glass at 3°C.

Sorption experiments were performed by equilibrating 0.1 g/L montmorillonite, 0.8 ppm carbon (as HA, FA, or DFOB) and $1 \times 10^{-10} \text{ M } ^{238}\text{Pu}$. Freshly prepared NaOH and HCl were used to control pH. Ionic strength was held constant at 10 mM using NaCl and NaHCO₃ and equilibrated with atmospheric conditions. Samples were shielded from light and equilibrated under gentle agitation at room temperature for the entirety of the experiment. Independent of pH, sorption of Pu(IV) to montmorillonite reached equilibrium after 1 month (supplementary Table 1). Ternary samples were initially prepared as binary systems of Pu-ligand or ligand-montmorillonite and allowed to equilibrate for 1 month. Either Pu(IV) or montmorillonite was added after the initial binary equilibration. Samples were then equilibrated as ternary systems for another month prior to sampling. Aqueous Pu concentrations were determined by centrifugation at 9200 g for 2 hours to remove solids (~50 nm cutoff), after which an aliquot of the supernatant was taken for analysis by liquid scintillation counting (LSC). Systems where Pu(IV) and an organic complexant were equilibrated prior to the addition of montmorillonite will be referred to as Pu(IV)-complexant-montmorillonite, while those

where the organic complexant was equilibrated with montmorillonite prior to the addition of Pu(IV) will be referred to as complexant-montmorillonite-Pu(IV) from here forward.

XRD and TEM characterization was performed on samples of 5 mg dry Na-montmorillonite dissolved in 1.0 mL of 0.01 M NaCl in the presence of DFOB. After a 24 hour equilibration, aliquots were rinsed three times with $>18\text{ M}\Omega$ water and placed on a zero background plate for XRD analysis or on a carbon coated copper grid for TEM analysis and air dried. XRD analysis was performed on a Bruker D8 X-ray diffractometer using radiation from a copper target tube ($\text{Cu } K_{\alpha}$) and operating at 40 kV, 40 mA and a scanning speed of $0.5^{\circ}/\text{min}$ while TEM analysis was performed on a Philips CM300 FEG super-twin microscope operating at 300 kV.

3.0 Results/Discussion

3.1 Binary sorption

Sorption of Pu(IV) to montmorillonite in the absence of any complexing ligand is shown in **Figure 2**. Sorption is greatest between pH 4 and 6 and decreases under alkaline conditions, which agrees with published K_d values (**Table 1**)¹⁰. The decrease in sorption at pH greater than 8 may be attributed to Pu(IV) hydrolysis and the formation of aqueous carbonate complexes. LaF_3 precipitation method was used to determine that the Pu remaining in solution after equilibrium was in the IV oxidation state at pH 8 and 10. There was insufficient Pu in solution at pH 4 and 6 for oxidation state analysis.

3.2 Pu Sorption in the Presence of Humic Acid

In the ternary system where HA was added, the sorption behavior at pH >6 was the same independent of the order of addition (**Figure 2A**). Although the order of addition was not significant, the presence of HA significantly decreased the total sorption of Pu to montmorillonite. At pH >6 , total Pu(IV) sorption to montmorillonite decreased by 20-50% relative to the binary system independent of the order of addition. At pH 6 a nearly 50% decrease in Pu(IV) sorption is observed. At pH >4 , a decrease in Pu(IV) sorption to montmorillonite observed in these experiments results from the greater stability of the Pu(IV)-HA aqueous complex relative to Pu(IV) surface species. The effect of HA decreases as aqueous carbonate species become more favorable at pH >8 (**Figure 3A**).

Similar decreases in Pu(IV) sorption was also observed in ternary experiments of HA-Pu(IV)-gibbsite at pH 6³⁴. In our experiments, the presence of HA strongly affected the behavior of Pu resulting in increased aqueous Pu concentrations.

At pH 4, Pu(IV) sorption to montmorillonite was not affected by the addition of HA. In these experiments, the surface sorption was near 100% for the binary system, and as a result we cannot determine if Pu(IV)-HA-montmorillonite ternary surface species played a role in Pu sorption. Precipitation of HA under these low pH conditions precludes any discussion of the nature of the sorbed Pu complex.

3.3 Pu Sorption in the Presence of Fulvic Acid

Sorption of Pu(IV) to montmorillonite in the presence of FA is shown in **Figure 2B**. Similar to the HA, altering the order of FA addition did not have a large effect on Pu(IV) sorption to montmorillonite. In both the Pu(IV)-FA-montmorillonite and FA-montmorillonite-Pu(IV) systems, there was only a minimal decrease in Pu(IV) surface sorption compared to the binary system at near neutral pH. No decrease in Pu(IV) sorption relative to the binary system was observed in the Pu(IV)-FA-montmorillonite system at neutral pH, though the overall trend remained consistent with our Pu(IV)-HA results. The FA-Pu(IV) aqueous complex is not predicted to be present at high pH (**Figure 3B**), though data on Pu(IV)-FA complexation is limited. Similar to our HA experiments, 100% Pu(IV) sorption was observed at pH 4. Ternary FA-metal-clay complexes have been shown to have no effect on metal sorption and no Pu(IV)-FA-clay species have been identified in the literature^{22, 26, 35, 36}. Humic acid decreased Pu(IV) surface sorption to a greater extent than FA at pH >4. This decrease is attributed to Pu(IV)-HA metal complexes being stronger than Pu(IV)-FA.

3.4 Pu Sorption in the Presence of Desferrioxamine B

Sorption of Pu(IV) to montmorillonite in the presence of DFOB is shown in **Figure 2C**. No effect on Pu(IV) sorption, compared to a binary system, was observed in the DFOB-montmorillonite-Pu(IV) system, indicating that the ligand is not out competing the montmorillonite for metal complexation (e.g. humic and fulvic acid systems). Pu(IV)-DFOB complexes are thermodynamically stable (**Table 1**) and predicted to be present over the range of pH studied (**Figure 3C**). However, the Pu(IV)-DFOB-montmorillonite

system shows an increase in sorption compared to the binary system. Unlike the FA and HA systems, the order of addition has a significant effect on the sorption of Pu(IV) to montmorillonite. Thus, different sorption processes are most likely controlling these two ternary systems and will be further discussed below.

In order to determine how DFOB interacts with montmorillonite, montmorillonite equilibrated with DFOB was further analyzed by XRD and TEM. **Figure 4** shows XRD patterns obtained from 3° to 10° (2 θ). In these diffraction patterns, a dominant peak and a broad shoulder can be identified occurring at low angle in the patterns of DFOB concentration lower than 1000 ppm (indicated by upward arrowheads). This indicates a broad range on interlayer spacing (supplementary Figure 1). The dominant peaks are representative of the basal spacing of the predominant clay, d_{001} , that can be determined according to Bragg's law:

$$2d\sin \theta = \lambda \quad (1)$$

where θ is the diffraction angle, d is the spacing of corresponding crystal plane, and λ is the wavelength of X-ray source (for Cu target: $\lambda (K_{\alpha 1,2}) = 1.5418 \text{ \AA}$). As the concentration of DFOB added to the system increased, from 0 to 10 ppm, the d_{001} peak shifted very slightly ($< 0.2^\circ$ in 2θ) to a higher diffraction angle (i.e., the basal spacing decreased) while the intensity of the broad pronounced shoulder decreased. At DFOB concentrations > 10 ppm, an increased basal spacing of d_{001} was observed with increasing of DFOB concentration. A maximum distance of 18.5 \AA occurred at 10000 ppm DFOB. An increase in basal spacing was also verified by TEM analysis. The selected-area diffraction patterns obtained from pure Na-montmorillonite and Na-montmorillonite equilibrated with 1000 ppm DFOB (**Figure 5**) match structures of clays with basal spacings of 12.7 \AA (montmorillonite-13 \AA) and 17.6 \AA (montmorillonite-18 \AA), respectively (see Supplementary Figure 2 for details). XRD and TEM results show no evidence of secondary mineral formation, suggesting the montmorillonite was not compromised during the experiment. Our results agree with previous studies that have observed significant sorption of DFOB by clays of up to $0.5 \text{ mmol}_{\text{DFOB}}/\text{mg}_{\text{Clay}}$ ^{21, 37}. At the relatively low DFOB mineral ratios used in our ternary Pu(IV) sorption studies, complete sorption of DFOB below pH 9 was expected. These results suggest that the DFOB is

contained primarily within the clay interlayer causing its expansion. Once DFOB is confined in the interlayer, it is not capable of complexing Pu. Both DFOB and Pu(IV)-DFOB remained in the clay interlayer over the time frame of these experiments.

The exact mechanism of DFOB accumulation in the montmorillonite interlayer remains undetermined, though previous studies of Fe(III), Cd(II), Cu(II), and Zn(II) have also observed an increase in metal sorption to montmorillonite in the presence of DFOB^{20,21}. The stability of the metal DFOB complex has been correlated to montmorillonite sorption, with stronger complexes showing greater affinity for sorption¹⁷. Pu(IV) DFOB complexes tend to be positively charged and they may be able to access the interlayer by a cation exchange mechanism. Such a sorption mechanism has been observed with structurally analogous Fe(III)-DFOB complexes^{21, 37}. Sorption of some inorganic cations may even exceed the a clays cation exchange capacity³⁸. Changes in DFOB structure, from linear to cyclical, upon complexation with Fe(III) and Pu(IV) may also increase its ability to access the interlayer^{17, 39, 40}. The Pu(IV) complexes of humic and fulvic acid are likely not able to access the interlayer as they are much larger and carry an overall negative charge.

4.0 Conclusions:

We have observed differences in Pu(IV) sorption to montmorillonite in the presence of organic matter that are dependent on pH, order of addition, and stability of metal ligand complex. In the HA and FA systems, there is minimal interaction of ligand and mineral and the Pu(IV) sorption processes are predominately controlled by competition between binary surface sorption and aqueous complexation. Sorption of DFOB appears to be controlled by interactions with the interlayer of montmorillonite. Due to the high intercalation affinity observed in these studies for DFOB and the Pu(IV)-DFOB complex, it appears likely they will remain irreversibly bound in the interlayer. The irreversible nature of DFOB accumulation in the montmorillonite interlayer also leads to an apparent dependence of Pu sorption on the order of addition. Broadly, it appears that the order of addition will be relevant in ternary systems in which at least one component exhibits irreversible sorption behavior. Importantly, if the Pu(IV)-DFOB complex is irreversibly

bound in the clay interlayer and inaccessible to desorption processes, colloid-facilitated Pu transport may be enhanced.

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Figure 1. Structure of desferrioxamine B mesylate (DFOB) salt.

Figure 2. Figure 2. Fraction of Pu(IV) sorbed onto 0.1 g/l montmorillonite in 0.01 M NaCl with 0.8 ppm C of A) Humic acid B) Fulvic acid C) Desferrioxamine B (DFOB). Black squares- binary sorption of Pu(IV) and Na-montmorillonite. Blue diamonds- complexant-montmorillonite- Pu(IV) system. Green triangles - Pu(IV)-complexant-montmorillonite system. Error bars represent 2σ off triplicate samples. Lines added for guidance.

Figure 3. Figure 3. Speciation diagram of 1×10^{-10} M Pu(IV) and 0.8 ppm of complexing ligands: A) Humic acid, B) Fulvic acid, and C) DFOB. Previously determined equivalence of charge of humic and fulvic acid were used to determine total number of binding sties and pKa's⁴¹ (supplementary table 2). Zero ionic strength thermodynamic data obtained from **Table 1** and NEA thermodynamic database vol 9. 2005.

Figure 4. X-ray diffraction patterns of 5 mg of Na-montmorillonite in 1.0 mL of 0.01 NaCl with 0 ppm DFOB (green), 5 ppm DFOB (mocha), 10 ppm DFOB (blue), 100 ppm

DFOB (red), 1000 ppm DFOB (purple) and 10000 ppm DFOB (yellow). See Supplementary Figure 1 for details.

Figure 5: Bright-field TEM images of pure Na-montmorillonite (A) and Na-montmorillonite equilibrated with 1000 mg/l of desferrioxamine B (B). (C) and (D) are selected-area electron diffraction patterns corresponding to images of (A) and (B), and match crystal structures of montmollonite-12.7 Å and montmollonite-17.5 Å, respectively (see Supplementary Figures 2 and 3 for details).

List of Tables:

Table 1. Thermodynamic constants for Pu(IV) interaction with organic ligands and mineral surface used in these studies. All stability constants are expressed at zero ionic strength unless noted in the table.

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